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IMPLANTATION-CONTROLLED DIFFUSION OF IMPURITIES
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TO THE FABRICATION OF MICROWAVE DEVICES

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Covering the period 1 May 1975
through 30 April 1978

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FOREWORD

The studies described here began on 1 May 1975 and were concluded on 30 April 1978. They are concerned with the introduction of impurities into III-V compound semiconductors by ion implantation and related processes: The research activity was conducted under the supervision of Professor J. F. Gibbons at the Solid State Electronics Laboratory at Stanford University, and led to the publication of one Ph.D. thesis, one Engineer's thesis and seven papers.

This is the Final Technical Documentary Report of the work under Contract ~~DAHC 75-G-0156~~.

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IMPLANTATION-CONTROLLED DIFFUSION OF IMPURITIES IN COMPOUND
SEMICONDUCTORS WITH APPLICATION TO THE FABRICATION
OF MICROWAVE DEVICES

Abstract

This report summarizes research carried out under Contract
DANCO4-75-6-0156.
~~DANC 75-6-0156.~~ The principal results obtained were as follows:

1. A double-layer encapsulant consisting of a layer of As-doped SiO_2 deposited on a layer of plasma-deposited Si_3N_4 was developed for annealing ion-implanted GaAs at temperatures up to 1100°C and InP at temperatures up to 900°C .

2. This encapsulant was used to study the properties of Se-implanted GaAs, with the following major results:

(a) Peak carrier concentrations of 10^{19} electrons/cm³ were obtained at annealing temperatures of 1100°C

(b) The solid solubility C_{ss} for Se in GaAs was measured and found to fit the expression

$$C_{ss} = 9.5 \times 10^{23} \exp(-1.23\text{eV}/kT) \text{ cm}^{-3}$$

(c) The ultimate carrier concentration from Se donors was found to be limited by solid solubility for Se concentrations below $10^{19}/\text{cm}^3$ and by degeneracy effects above this level

(d) A model for Se diffusion in GaAs was developed involving the simultaneous diffusion and interaction of four chemical species of Se in GaAs: (i) substitutional Se; (ii) interstitial Se; (iii) Se complexed with a Ga vacancy, and (iv) precipitated Se.

3. The two layer encapsulant was also used to study the annealing behavior of S-implanted Cr-doped InP at temperatures up to 900°C , in which an electrical activity of 68% was obtained on a sample implanted to a dose of 10^{14} S/cm^2 at 120 keV and annealed at 900°C for 20 minutes.

4. A two layer encapsulant composed of an evaporated layer of Ga_2S_3 covered by an evaporated layer of SiO_2 was developed to solve special problems that arise in the annealing of S-implanted GaAs. 100% electrical activity was obtained for ion doses up to 10^{13} /cm^2 , annealed at 825°C for 10 minutes.

CHAPTER I

This report summarizes research that was performed under
Contract ~~DAHC 75-3-0156~~ ^{DANCO4-75-G-0156} at Stanford University during the
period 1 May 1975 to 30 April 1978. The research was directed
toward the development of improved encapsulants for annealing
ion-implanted III-V compound semiconductors, particularly GaAs
and InP.

The need for improved encapsulants arises from the following
experimental observations. First, in GaAs, an encapsulant that
will not dissolve Ga nor permit As to escape is required. Several
investigators have shown that a thin layer (1000 Å) of Si_3N_4 is
suitable for this purpose at annealing temperatures up to $\sim 900^\circ\text{C}$,
but that at higher annealing temperatures the encapsulant tends
to pit and blister and severe surface deterioration of the GaAs
results. At the same time, electrical activity of implanted
n-type dopants in GaAs (S, Se, Te) is a monotonically increasing
function of temperature in the range $700^\circ\text{--}900^\circ\text{C}$, suggesting that
improved electrical activity and carrier mobility can be obtained
if annealing can be carried out at higher temperature.

These considerations led us to develop a two layer encapsulant
composed of a 1000 Å layer of plasma-deposited Si_3N_4 covered by
a 1 μm layer of As-doped SiO_2 . This encapsulant was found to
permit annealing of ion-implanted GaAs at temperatures up to 1100°C
with no signs of mechanical failure and improved electrical
activity and carrier mobility. The higher annealing temperatures

made possible by this encapsulant also provided the means to study the solid solubility of Se in GaAs at high temperatures and the mechanism for diffusive redistribution of Se in GaAs during annealing. These results are described in the papers listed as references 1-6 and in the Ph.D. thesis of Alexander Lidow. Because the thesis is lengthy, only the abstract is reproduced as Chapter II of this report. A copy of the thesis is on file with the Army Research Office, Durham.

A special problem arises in the annealing of S-implanted GaAs, even with the encapsulant described above, due to the fact that S tends to dissolve in the Si_3N_4 layer. To prevent this problem, a special $\text{Ga}_2\text{S}_3/\text{SiO}_2$ encapsulant was developed which provides excellent surfaces after annealing, no sulfur out diffusion during annealing, and high electrical activity at anneal temperatures up to 825°C . Because of this limited temperature range, high electrical activity is only obtained for sulfur doses less than $\sim 2 \times 10^{13}/\text{cm}^2$, though these doses are sufficient for fabrication of active layers in microwave GaAs FETs and other such devices.

A full description of the encapsulation technique and the annealing results is given in the Engineer's thesis of Elie S. Ammar. Due to the length of this thesis, only the abstract is reproduced here as Chapter III. The complete thesis is on file at the Army Research Office, Durham.

The final piece of research work sponsored under the subject contract was concerned with the development of a two-

layer encapsulant for annealing S-implanted Cr-doped InP.

For this case, a 1000 Å thick Si_3N_4 layer covered by a 1 μm layer of phosphorus-doped SiO_2 (PSG) was found to be useful for post-implantation annealing of S-implanted InP at temperatures up to 900°C without surface deterioration.

The results of this research have been accepted for publication in the Journal of Applied Physics. A pre-publication copy of the journal article has been filed with the Army Research Office, Durham. The abstract of the paper is included in this report as Chapter IV.

CHAPTER II

ENCAPSULATION AND ANNEALING OF ION IMPLANTED SELENIUM IN GaAs

Abstract

A method is described by which GaAs may be encapsulated to withstand annealing temperatures over 1100°C using a double layered encapsulant consisting of arsenic doped silicon dioxide on top of plasma deposited silicon nitride. Samples encapsulated in such a manner and annealed show no signs of mechanical failure and yield higher electrical activation of ion implanted selenium when compared with samples annealed with silicon nitride only. In addition, there is no detectable outdiffusion of Ga or As and no detectable infussion of Si. Peak electrical activation of ion implanted Se has been measured a 1.0×10^{19} carriers/cm³ for samples annealed at 1100° C. A first order strain analysis of general multilayered systems is also presented, indicating possible improvements on such an encapsulating procedure for GaAs as well as other compound semi-conductors. The development of this encapsulant is shown to be essential for the study of diffusion of ion implanted elements in GaAs such as selenium.

Electrical measurements are combined with the technique of secondary ion mass spectrometry (SIMS) in order to experimentally analyze and correlate the diffusion and activation of ion implanted selenium in GaAs. Four chemically different species of selenium are identified: (1) substitutional selenium, (2) interstitial

selenium, (3) selenium complexed with a gallium vacancy, and (4) precipitated selenium. It is the interactions between these four that dictates resulting redistribution and electrical activation of implanted layers. The factors governing these interactions are investigated, and it is demonstrated that only substitutional selenium is a shallow donor. In addition, it is shown that the species responsible for redistribution of impurity profiles is the selenium-gallium vacancy complex. Precipitated and interstitial selenium appear to neither diffuse nor act like donors in GaAs.

A model is developed which formalizes these observations in a set of five coupled differential equations. By employing a minimum number of simplifying assumptions, we are able to extract quantitative predictions from this model which accurately describe not only our experimental results but those of other workers.

The above abstract is from the Ph.D thesis of Dr. Alexander Lidow. Five technical papers [1-5 in the attached list] have been published from this work.

Dr. Lidow is now employed at the International Rectifier Corporation.

CHAPTER III

IMPLANTATION AND ANNEALING OF SULFUR IN GALLIUM ARSENIDE

Abstract

A new method for the encapsulation of sulfur-implanted GaAs has been developed. It solves the problem of sulfur outdiffusion during annealing. This method uses a two-layer cap: a 6000 Å layer of evaporated Gallium Sulfide (Ga_2S_3) followed by a 2000 Å layer of evaporated Silicon Dioxide. This cap can stand annealing temperatures of 825°C, and can result in excellent surfaces after annealing. It succeeds in preventing sulfur outdiffusion and results in high electrical conversion of the implanted layer.

The above abstract is from the Engineer's Thesis of Mr. Elie S. Ammar. Oral presentation of the work was given at the International Conference on Ion Implantation in Boulder, Colorado in August 1976.

Mr. Ammar is now employed at Advanced Microsystems Incorporated.

CHAPTER IV

ION IMPLANTATION OF SULFUR IN Cr-DOPED InP AT ROOM TEMPERATURE

Abstract

A double-layer encapsulant of phosphorous glass (PSG)/Si₃N₄ is shown to be useful for post-implantation annealing of sulfur-implanted InP up to 900°C without surface deterioration. Under high dose implantation and high temperature annealing conditions, however, a highly conductive layer is formed near the surface of the InP. A highly compensated or p-region is also produced in the deeper part of the implanted layer. The existence of both thermally-induced and damage-induced conductivity must be taken into account to estimate the electrical activity of implanted species from sheet carrier concentration. An estimated real electrical activity of sulfur implanted into InP at room temperature has been established by subtracting damage-induced carrier concentration obtained from argon implantation data. A maximum electrical activity of 68% was obtained on a sample implanted to a dose of $1 \times 10^{14} \text{ S}^+/\text{cm}^2$ and annealed at 900°C for 20 minutes.

The above abstract is from a paper that has been accepted for publication in the Journal of Applied Physics (Ref. 6).

Mr. Kasahara was on leave at Stanford from the SONY Corporation during the period that this study was performed. He has since returned.

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7. Anomalous Gate Capacitance in GaAs FETs, H. F. Cooke, J. F. Gibbons, W. Gelnovatch (submitted to IEEE Transactions on Electron Devices - September 1977).

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